

Thermal effects on the process of electropolymerization of pyrrole on mild steel

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Received 29 August 2002; received in revised form 14 April 2003; accepted 30 May 2003

Abstract

Polypyrrole films were electrosynthesized on mild steel with oxalic acid electrolyte at varying temperatures (25–65 °C), current density (0.5–6.0 mA/cm²) and pH (2.0, 4.0, 7.0 and 8.5). The concentrations of pyrrole and oxalic acid were maintained at 0.1 M each in galvanostatic experiments. The results show that lower temperatures favor the formation of polypyrrole on mild steel in acidic media. At higher temperature and lower current densities, oscillations in electrode potentials were observed. The film quality was poorest at pH 7.0, while very adherent and compact films were obtained in alkaline medium. Higher temperature in alkaline media favors the formation of better polypyrrole films in contrast with acidic media.

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Keywords: Electropolymerization; Mild steel; Polypyrrole films

1. Introduction

The electropolymerization of pyrrole on oxidizable metals (e.g. Fe, Zn, Pb, etc.) is difficult as the metal dissolution potentials are much lower than the oxidation potential of pyrrole. The metal dissolution dominates and polymerization does not take place at all or very loosely adherent films are formed in some cases. The problem, in principle, can be solved by selecting appropriate supporting electrolyte, pretreating the metal surface, and/or varying polymerization parameters, e.g. concentration of monomer, concentration of electrolyte, pH of the electrolyte and current density. However, these changes will be associated with change in the conductivity and morphology of the film. For iron and mild steel several ways of overcoming this problem have been investigated. Troch-Nagels et al. [1] used Na₂SO₄ solution as supporting electrolyte. It demonstrated good corrosion resistance but exhibited poor adhesion and films were brittle. Schirmeisen and Beck [2] observed similar characteristics with Na₂SO₄ solution. Beck et al. [3] deposited polypyrrole on iron from aqueous solutions of pyrrole and oxalic acid which yielded strongly adherent and smooth polymer layers. De Bruyne et al. [4] electropolymerized pyrrole on galvanized steel substrates prior to a pretreatment

with a solution of 0.1 M sodium sulfide. The adherence of polypyrrole film was greatly enhanced by Ferreira et al. [5] through electropolymerization of pyrrole on pretreated iron and mild steel. Pretreatment by 10% aqueous nitric acid inhibited the metal dissolution without preventing the pyrrole oxidation. Su and Iroh [6–12] formed polypyrrole coatings on stainless steel using aqueous benzene sulfonate solution as electrolyte. The effect of various parameters on electropolymerization was studied. It was found that amount of polypyrrole formed during electropolymerization increased with current density and monomer concentration, but was unaffected by increased electrolyte concentration. Krstajic et al. [13] used oxalic acid solution as supporting electrolyte and studied resulting corrosion protection in acid sulfate solutions. The change in open circuit potential with respect to time for various thickness of polypyrrole coating was observed. Idla et al. [14] electropolymerized pyrrole from sodium *p*-toluenesulphonate (ToS) water–ethanol solution. Reut et al. [15] synthesized polypyrrole films from the aqueous solution of pyrrole and sodium *p*-toluenesulphonate (Py/ToS). A one step electrosynthesis of polypyrrole films on zinc substrates was done by Aeiyaeh et al. [16]. This was achieved by electro-oxidation of pyrrole in aqueous oxalate solution containing small amounts of sulfide ion at pH 5 in either the galvanostatic or potentiodynamic modes.

Ba-Shammakh [17] has recently compared some of these methods and found that Beck's method [3] gives uniform and adherent polypyrrole film with fewer defects. The method

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has been studied by Su and Iroh [7] in details. They investigated effects of electrochemical process parameters such as pH of the reaction media, applied current density and initial monomer (pyrrole) and electrolyte (oxalic acid) concentrations on the formation process of polypyrrole coatings. The temperature, which is generally not studied as a parameter in electrochemical synthesis reactions, is in fact, an important variable as it accelerates the kinetics. The electropolymerization of pyrrole in aqueous medium involves at least two electrochemical reactions and mass transfer of pyrrole from bulk to the surface. The objective of the present work is to study effect of temperature along with applied current density and solution pH, on the process of electropolymerization of pyrrole on mild steel. It is of academic importance to know how the temperature affects the over all process. The results of this study will be helpful to select the range of parameter for better and economic deposition of the polypyrrole on mild steel, a process which is currently being evaluated for corrosion protection.

2. Experimental

The electropolymerization is done in an electrochemical cell with a flag shape mild steel coupon, on which pyrrole is desired to polymerize, functioning as working electrode. A stainless steel bar and saturated calomel electrode (SCE) worked as counter and reference electrodes, respectively. These three electrodes were connected to a potentiostat (EG&G PARC model 273A) via an electrometer. The potentiostat was controlled through an electrochemical software (M270, EG&G PARC) from an IBM compatible microcomputer.

The cell has jacketed body that allows circulation of hot/cold water so that a desired temperature is maintained during the electropolymerization. The temperature was recorded using a thermometer of 0.1 °C least count. The pH of the electrolyte was measured by a calibrated pH meter. The pH was adjusted by adding NaHCO₃. Analytical grade chemicals were used as received, except pyrrole, which was purified by silica gel bed. The solutions were made in deionized water.

Mild steel coupons of predetermined size in flag shape (1 cm × 1 cm) were machined from a mild steel sheet of 1 mm thickness. The coupons were first cleaned mechanically with increasing grades of emery papers with grit size 100, 400, 600 and 1500. Subsequently, a wash with acetone removed any oil or grease. The stem of the coupon was insulated with an insulating paint such as to expose the desired deposition area. Fifty milliliters of the prepared solution were used in each experiment. All three electrodes were placed vertically in the cell. The temperature and the pH were measured. The deposition was done galvanostatically through chronopotentiometry, one of the pre-designed experiments in the software M270.

Table 1
Values of various parameters in the experiments

Parameters	Value
Pyrrole concentration (M)	0.1
Electrolyte concentration (M)	0.1
Time of deposition (s)	1800
Temperature (°C)	25, 35, 45, 55, 65
Current density (mA/cm ²)	0.5, 2.0, 4.0, 6.0
pH	2.0, 4.0, 7.0, 8.5

The concentrations of pyrrole and oxalic acid were held constant in all runs while the temperature, pH and applied current densities have been changed. The values of the parameters are given in Table 1. After each experiment, the coated steel sample was rinsed with water and dried in a vacuum oven at 50 °C to obtain constant weight. The deposited polypyrrole film was tested for adherence and surface uniformity and morphology. Surface adherence was tested qualitatively by scratching with stainless steel spatula. The surface uniformity and morphology were determined by obtaining scanning electron micrographs (SEM).

3. Results and discussion

A typical galvanostatic electropolymerization gives chronopotentiometric curve as shown in Fig. 1. The process evidently has two distinct stages. In the first stage the electrode potential remains constant and negative (e.g. approximately –500 mV SCE at pH 2.0 and 25 °C). The potential corresponds to the acidic dissolution of iron. This stage is termed as induction and the duration as induction time. During this stage acidic dissolution of iron takes place till sufficient corrosion products, needed for surface passivation, have been formed. The iron dissolution slows down and eventually stops as the oxidation of pyrrole starts as soon as the surface is passive. This stage could be termed as pyrrole oxidation stage. Its initiation is manifested by a sharp peak at the end of induction period. Both of these stages are affected by process parameters, namely, monomer (pyrrole) concentration, electrolyte (oxalic acid) concentration, time of deposition, current density in galvanostatic mode, applied potential in potentiostatic mode, surface pretreatment and pH of the solution.

Su and Iroh [7] have studied the effects of current density, monomer concentration, electrolyte concentration and solution pH at room temperature. In the following sections, the effect of temperature on electropolymerization process has been discussed.

3.1. In acidic media

3.1.1. Electropolymerization at 25 °C

Chronopotentiometric plots of polypyrrole deposition at 2.0 pH and 25 °C are shown in Fig. 2. When the applied

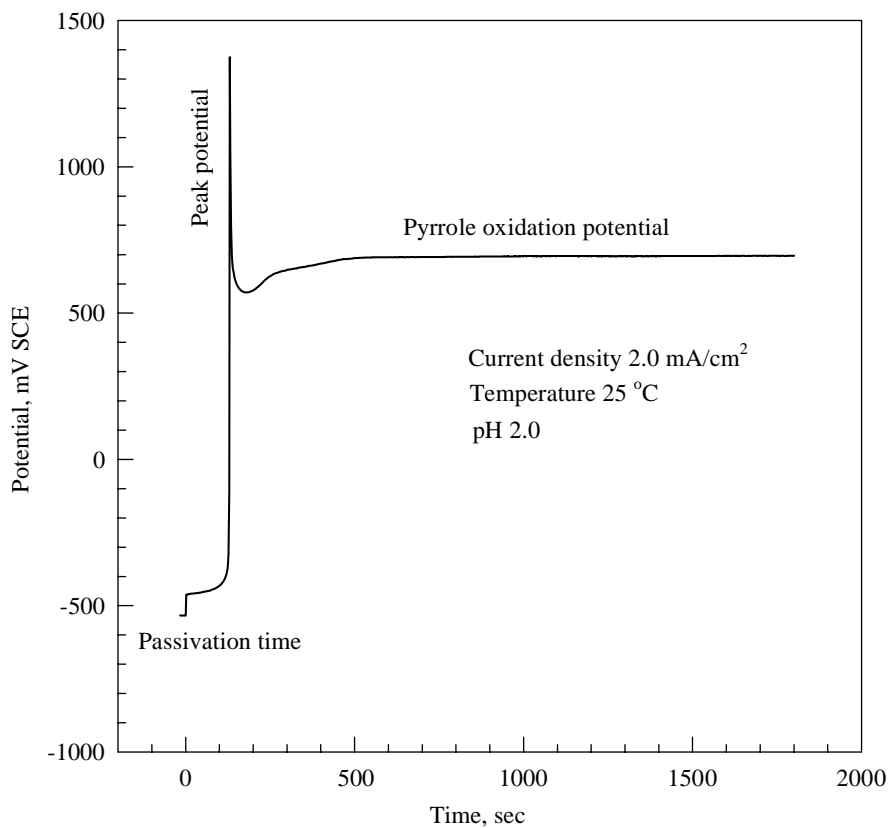
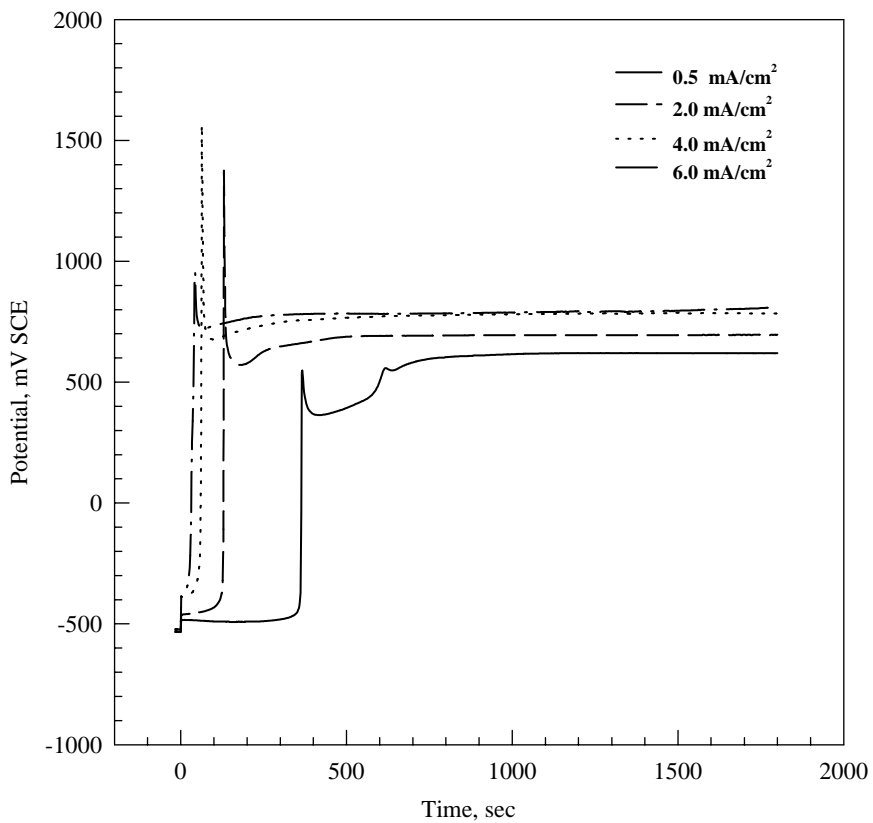


Fig. 1. A typical potential–time curve.

Fig. 2. Potential vs. time at pH 2.0 and $T = 25\text{ }^{\circ}\text{C}$.

current density was 0.5 mA/cm², the polymer film was very thin and it was difficult to determine whether it was due to corrosion product or polypyrrole. Since an expected plot was observed, it was inferred that it was a thin polypyrrole film. At 2.0 mA/cm² current density, a perceptible black film was observed and the film surface was smooth. Increasing current density resulted into compact and adherent film. However, at 6.0 mA/cm², the surface became rough but film was adherent. Some pinholes were also observed. The roughness of surface at higher current density was also observed by Su and Iroh [7]. It was suggested that the roughness is due to some side reactions. The reactions were not mentioned. Nevertheless, the increased surface roughness with higher current density could be because of higher polymerization rate. As the rate of polymerization increases, orderliness of deposition decreases which is observed as increased roughness.

The oxidation potential increases with increased current density as expected in any kinetics controlled electrochemical reactions. However, the induction time decreased sharply with current density. The induction time (τ) was 357.8 s at 0.5 mA/cm², while it was only 27.2 s at 6.0 mA/cm² for the same temperature and pH (cf. Table 2). A linear regression of these data at pH 2.0 results into:

$$\ln(\tau) = 5.29 - 1.0 \ln(i) \quad (R^2 = 0.9730) \quad (1)$$

This equation is comparable with the equation of Su and Iroh [7] with pyrrole concentration of 0.25 M at pH 2.4:

$$\ln(\tau) = 5.22 - 1.16 \ln(i) \quad (2)$$

It seems that a certain amount of corrosion products are required to achieve sufficient degree of passivation needed for successful deposition of pyrrole on iron. It takes longer to obtain the required degree of passivation at lower current densities.

Chronopotentiometric plots of polypyrrole deposition at pH 4.0 and 25 °C are shown in Fig. 3. The polymer film was very thin at 0.5 mA/cm², like the one obtained at 2.0 pH. At higher current density, adherent, black films were observed. The film surfaces were relatively smoother than those obtained at 2.0 pH using same current densities. Apparently, at higher pH, the rate of pyrrole oxidation is lesser which provides orderliness in the process of polymerization that resulted in smoother surface.

The induction time at pH 4.0 is generally higher than those at pH 2.0 as shown in Table 2. It is known that the rate of iron dissolution in acidic media becomes less as pH is increased [18]. With slower reaction, it takes more time to achieve the required degree of passivation for initiation of pyrrole oxidation. The induction time decreases with current density following a power law equation. A linear fit on logarithmic scales gives following equation:

$$\ln(\tau) = 6.24 - 1.32 \ln(i) \quad (R^2 = 0.9903) \quad (3)$$

At higher current densities, e.g. 4.0 and 6.0 mA/cm², the oxidation potentials increase with time, when pH was maintained at 4.0. The increase in oxidation potential with time at pH 6.0 and at 5.63 mA/cm² was also observed by Su and Iroh [7]. This phenomenon is not well understood. Nevertheless, an increase in potential with time could be explained if the conductivity of film is significantly low. In this case additional uncompensated potential in the film will be manifested as increased potential. The constant potential at lower current densities and also at higher current densities at pH 2.0 could be due to thinner film and higher film conductivities.

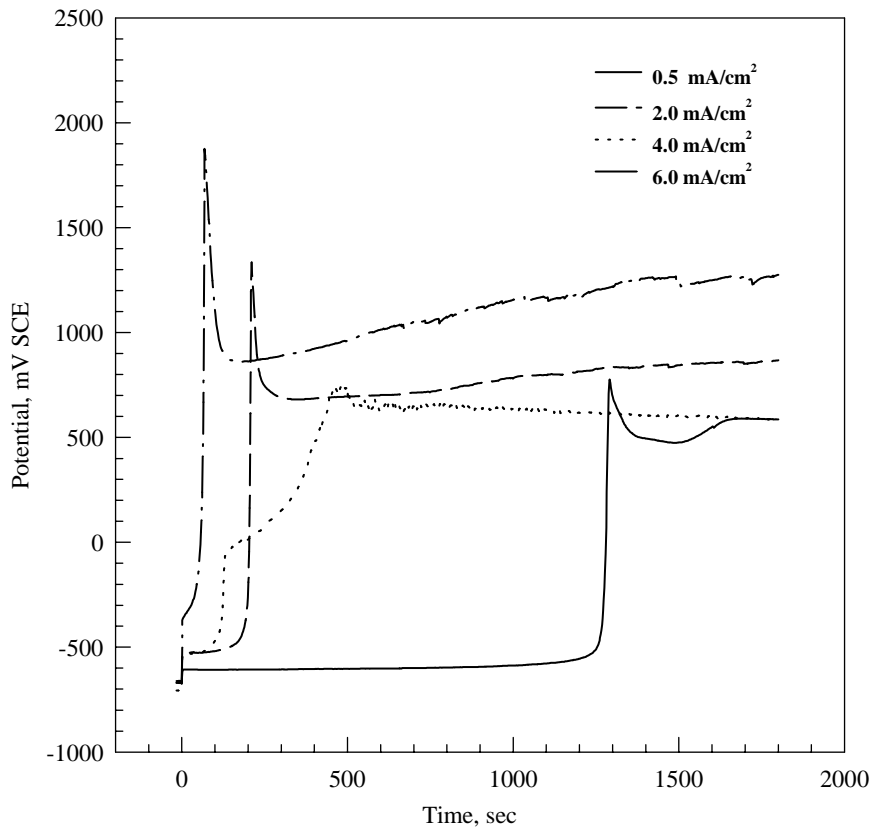
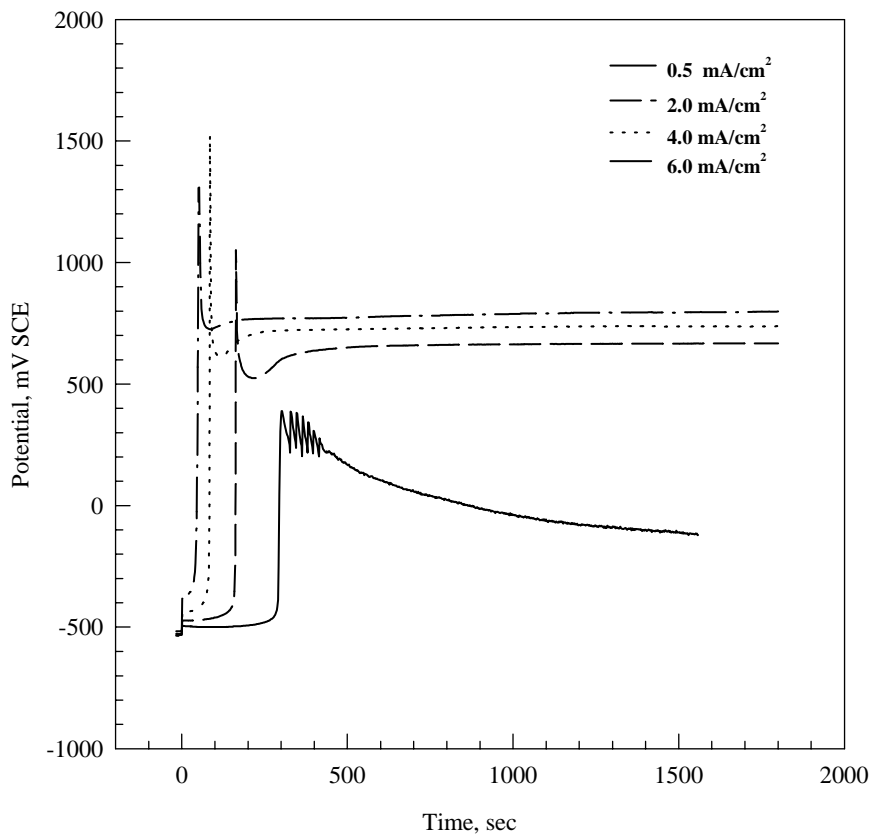
3.1.2. Electropolymerization at higher temperatures

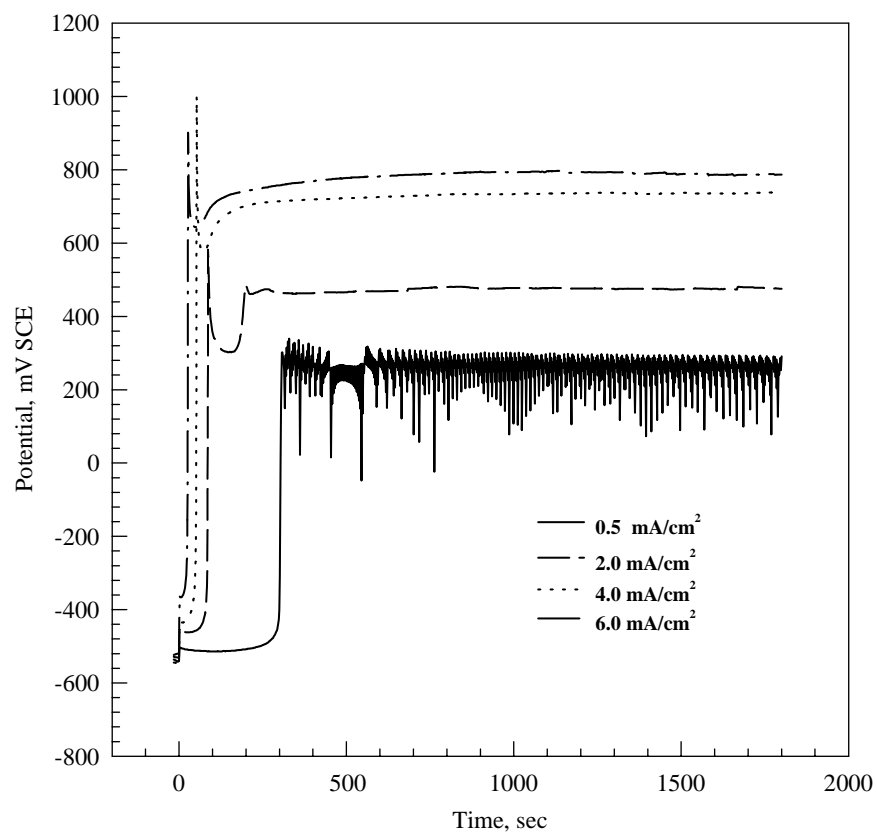
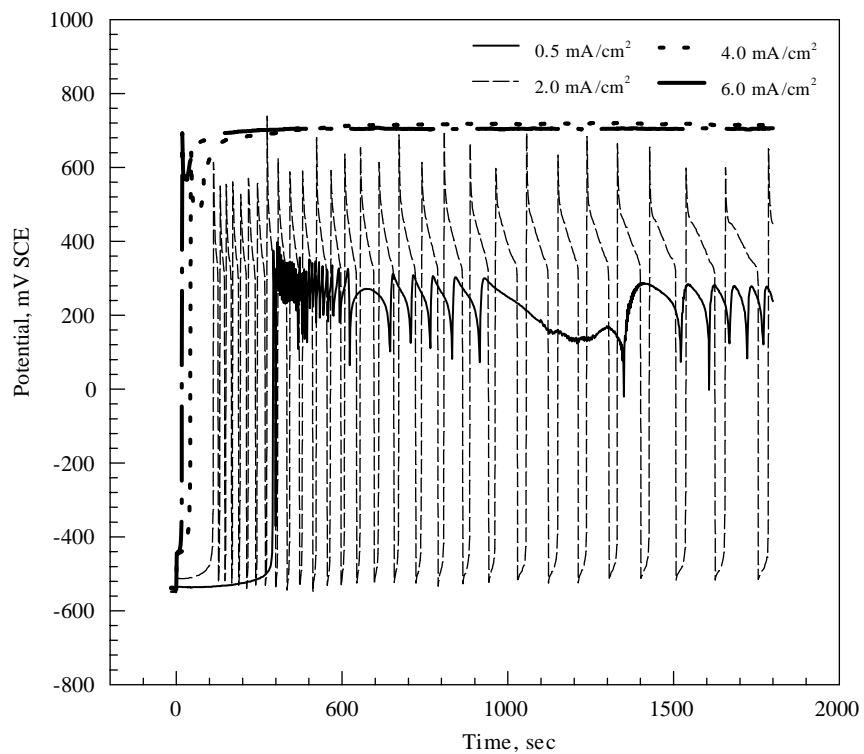
Chronopotentiometric plots of polypyrrole deposition at 2.0 pH and higher temperature (i.e. 35, 45, 55 and 65 °C) shown in Figs. 4–7 exhibit similar trends except oscillations. At 35 °C, a very thin polypyrrole film was observed when the applied current density was 0.5 mA/cm². A better deposition was noticed at higher current density, e.g. 2.0 and 4.0 mA/cm². However, pinholes and rough surface were observed at 6.0 mA/cm² current density (cf. Fig. 8). The same observations were made even at higher temperature. It was interesting to note that thinner polypyrrole films were formed as temperature was increased at a given current density. In fact, no films were formed at lower current densities (0.5 and 2.0 mA/cm²) at 55 and 65 °C. It appears that the kinetics of both reactions, i.e. the iron dissolution and oxidation of pyrrole, were improved with temperature. But increase in the rate of iron dissolution was much higher than that of polypyrrole formation. It can be concluded that overall process is favored by lower temperature in acidic media (pH 2.0 and 4.0).

At all higher temperatures, the oxidation potential increases with increased current density similar to at room

Table 2
Induction time τ (s) at different temperatures and current densities in acidic and neutral media

Current density (mA/cm ²)	Temperature (°C)														
	25			35			45			55			65		
	pH 2.0	pH 4.0	pH 7.0	pH 2.0	pH 4.0	pH 7.0	pH 2.0	pH 4.0	pH 7.0	pH 2.0	pH 4.0	pH 7.0	pH 2.0	pH 4.0	pH 7.0
0.5	357.8	1264.0	>1800	570.3	1497.0	>1800	299.7	14.0	>1800	294.3	1769.0	>1800	243.4	408.7	>1800
2.0	121.7	194.4	835.5	161.7	145.3	>1800	79.9	499.5	1144.0	105.3	405.0	>1800	78.1	90.8	>1800
4.0	54.5	99.9	461.4	76.3	59.9	550.5	50.9	223.4	848.2	40.0	178.0	1228.0	29.1	61.8	1722.0
6.0	27.2	41.8	319.0	36.0	32.7	323.3	25.4	127.1	83.6	29.1	90.8	278.0	14.5	47.2	940.4

Fig. 3. Potential vs. time at pH 4.0 and $T = 25^{\circ}\text{C}$.Fig. 4. Potential vs. time at pH 2.0 and $T = 35^{\circ}\text{C}$.

Fig. 5. Potential vs. time at pH 2.0 and $T = 45^{\circ}\text{C}$.Fig. 6. Potential vs. time at pH 2.0 and $T = 55^{\circ}\text{C}$.

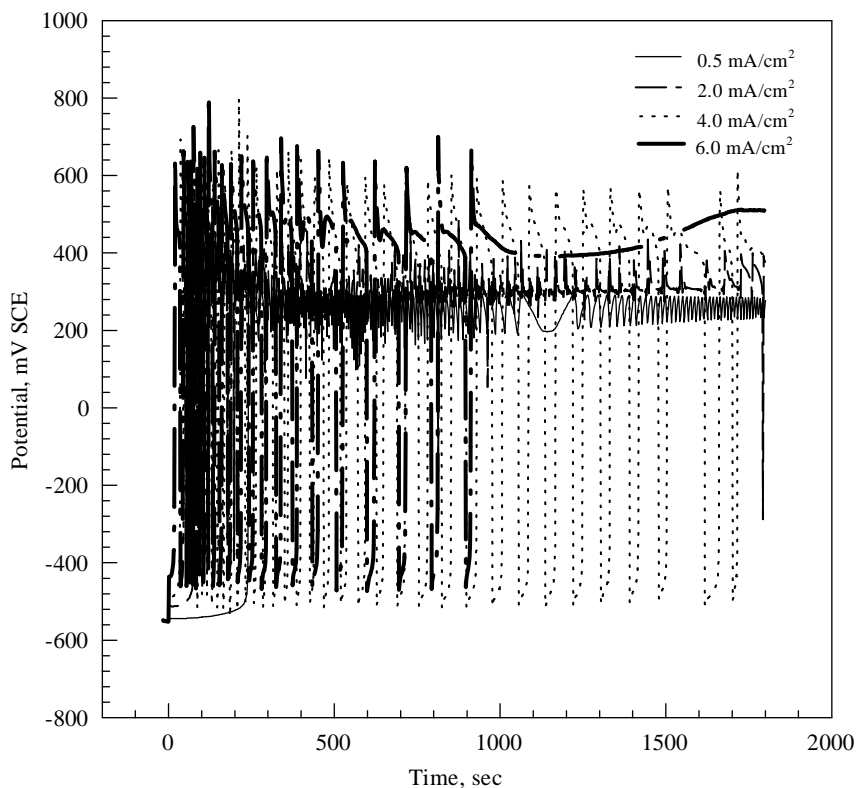


Fig. 7. Potential vs. time at pH 2.0 and $T = 65^\circ\text{C}$.

temperature. The induction time decreased with increased current density for the whole range of temperatures as shown in Table 2. The temperature does not seem to have significant effect on the induction time. Regression of the data yield following expressions at different temperatures in the electrolyte of pH 2.0:

$$\ln(\tau) = 5.69 - 1.07 \ln(i) \quad \text{for } T = 35^\circ\text{C} \quad (R^2 = 0.9817) \quad (4)$$

$$\ln(\tau) = 5.10 - 0.95 \ln(i) \quad \text{for } T = 45^\circ\text{C} \quad (R^2 = 0.9844) \quad (5)$$

$$\ln(\tau) = 5.10 - 0.95 \ln(i) \quad \text{for } T = 55^\circ\text{C} \quad (R^2 = 0.9813) \quad (6)$$

$$\ln(\tau) = 4.85 - 1.10 \ln(i) \quad \text{for } T = 65^\circ\text{C} \quad (R^2 = 0.9710) \quad (7)$$

Potential–time curves of polypyrrole coating at pH 4.0 and higher temperatures are shown in Figs. 9–12. The observations were very similar to those at pH 2.0. The film surfaces obtained at pH 4.0 were smoother than those obtained at pH 2.0. For the same applied current density, increasing the temperature would result into smooth but thin polypyrrole deposition. This may be due to high dissolution rate and low polymerization rate at high temperature. The deposition was not good at 0.5 mA/cm^2 at high temperatures. Increasing the

current density gives more adherent polypyrrole film but the surface becomes rough when the applied current density was 6.0 mA/cm^2 .

The induction time at pH 4.0 is generally higher than obtained at pH 2.0 for the same temperature. The dissolution rate of iron is low at high pH, therefore more time was required to get sufficient passivation as pH increased. Increasing the temperature did not have significant effect on the induction time especially at high current density. For example, the induction time was 55 s at 35°C , while it was 60 s at 65°C for the same applied current density (cf. Table 2). Logarithm of induction time gives good linear fit with logarithm of current density for all temperatures at pH 4.0:

$$\ln(\tau) = 6.19 - 1.53 \ln(i) \quad \text{for } T = 35^\circ\text{C} \quad (R^2 = 0.9967) \quad (8)$$

$$\ln(\tau) = 7.00 - 1.23 \ln(i) \quad \text{for } T = 45^\circ\text{C} \quad (R^2 = 0.9976) \quad (9)$$

$$\ln(\tau) = 6.71 - 1.20 \ln(i) \quad \text{for } T = 55^\circ\text{C} \quad (R^2 = 0.9935) \quad (10)$$

$$\ln(\tau) = 5.32 - 0.87 \ln(i) \quad \text{for } T = 65^\circ\text{C} \quad (R^2 = 0.9784) \quad (11)$$

The oxidation potential has tendency to increase with time especially at 45 and 55°C for high current density, e.g. 2.0, 4.0 and 6.0 mA/cm^2 as also observed at pH 2.0.

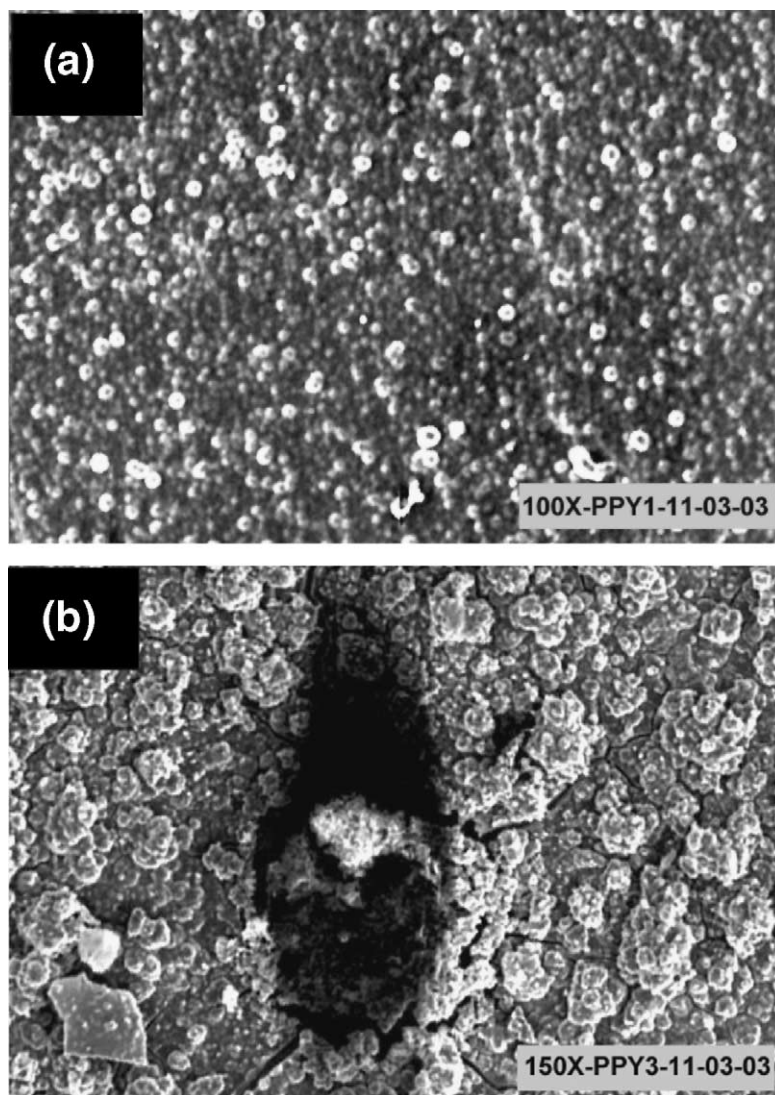


Fig. 8. SEM of polypyrrole films deposited at 25 °C, pH 2.0 and at (a) with 2 mA/cm²; and (b) 6 mA/cm² current densities.

3.1.3. Oscillations in electrode potential

Oscillations in electrode potential were observed during the electropolymerization of pyrrole, at combinations of higher temperatures and lower current densities. The instances of oscillations are summarized in Table 3. The nature, periodicity and amplitude varied greatly with parameters. It is indicative of the presence of some sort

of instability. The oscillations in current were also observed by Petitjean et al. [19], while potentiostatic electropolymerization of pyrrole in aqueous solution containing tetrabutylammonium-hexafluorophosphate. A mechanism was proposed based on the considered electrolyte system.

The instability in electrode potential in our experiment can be explained on the basis of hypothesis of two competing

Table 3
Oscillations instances

Current density (mA/cm ²)	Temperature (°C)										
	25		35		45		55		65		
	pH 2.0	pH 4.0	pH 2.0	pH 4.0	pH 2.0	pH 4.0	pH 2.0	pH 4.0	pH 2.0	pH 4.0	
0.5	–	–	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
2.0	–	–	–	–	–	–	Yes	–	Yes	–	Yes
4.0	–	–	–	–	–	–	–	–	Yes	–	Yes
6.0	–	–	–	–	–	–	–	–	Yes	–	Yes

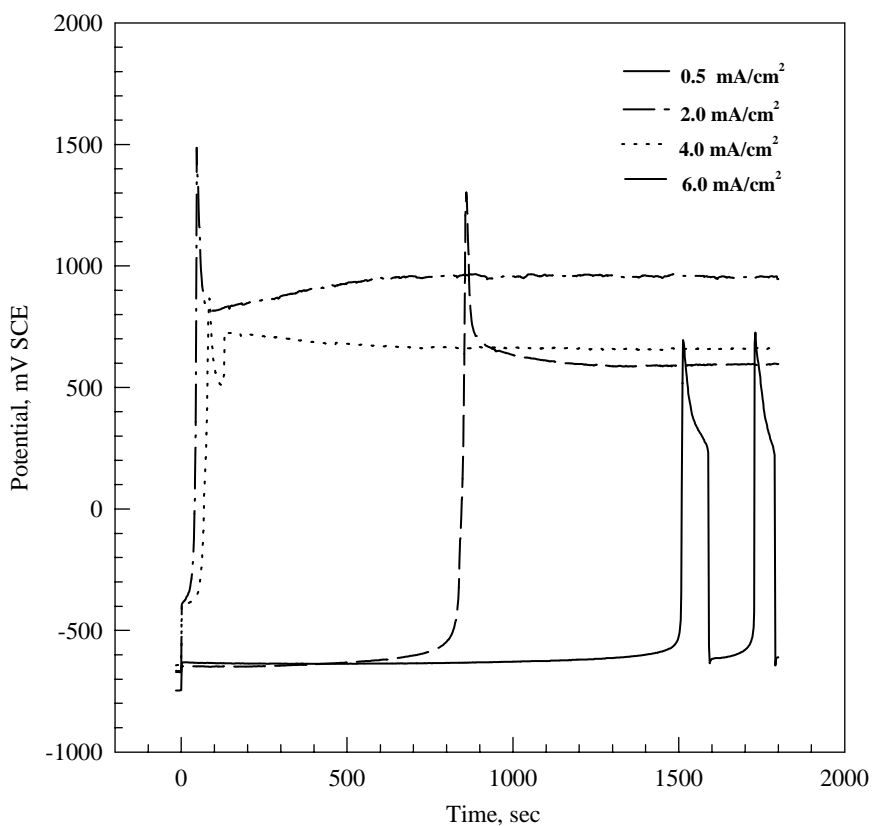


Fig. 9. Potential vs. time at pH 4.0 and $T = 35\text{ }^{\circ}\text{C}$.

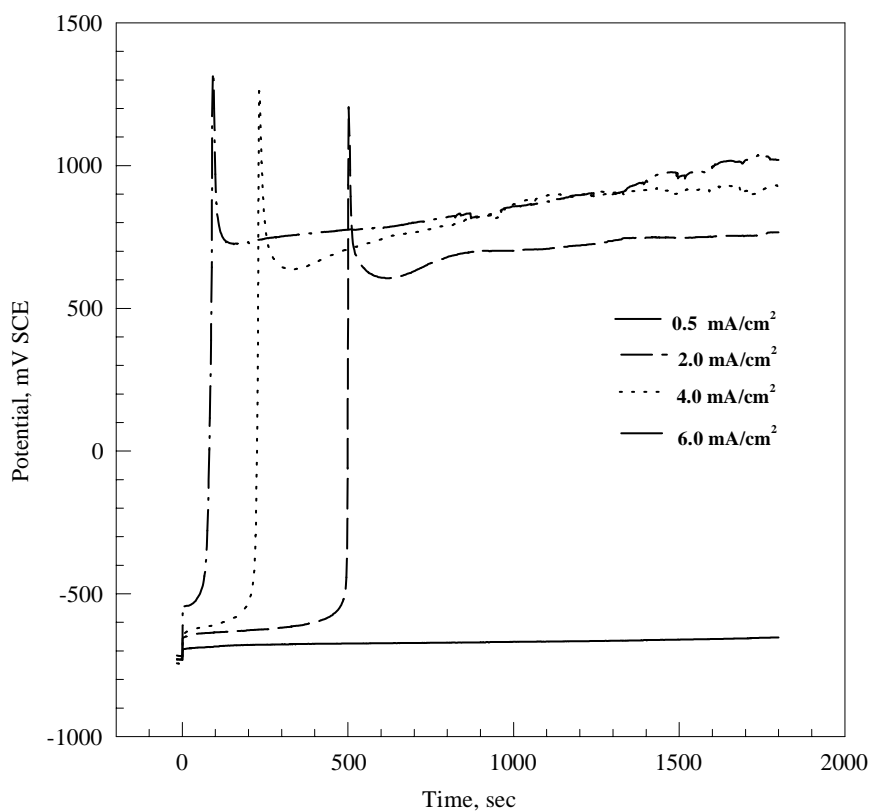
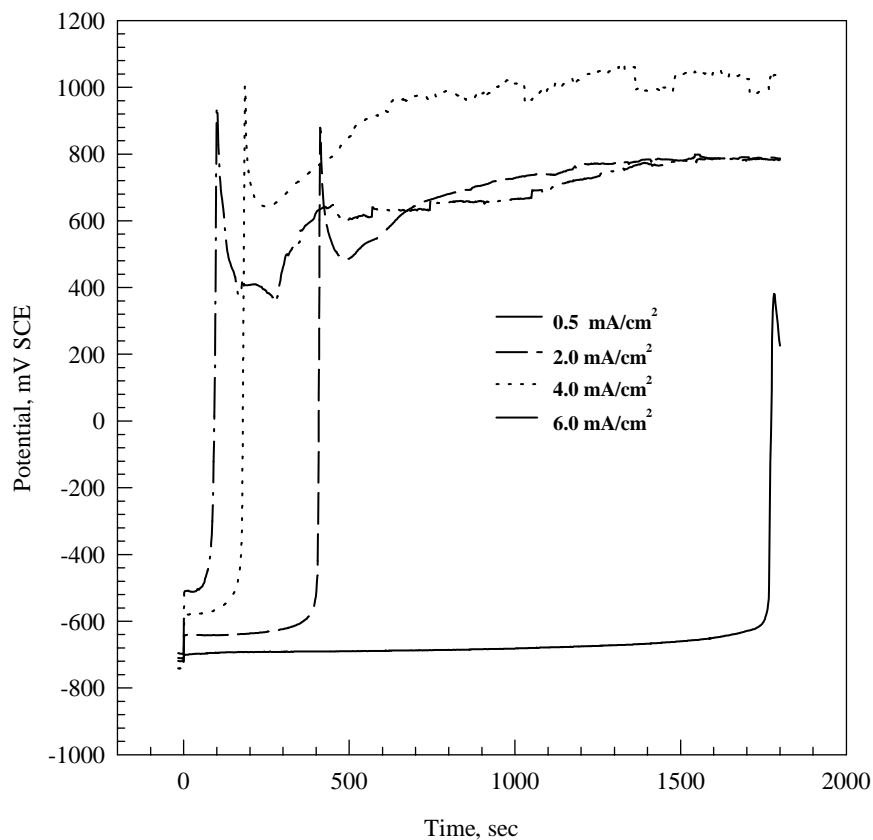
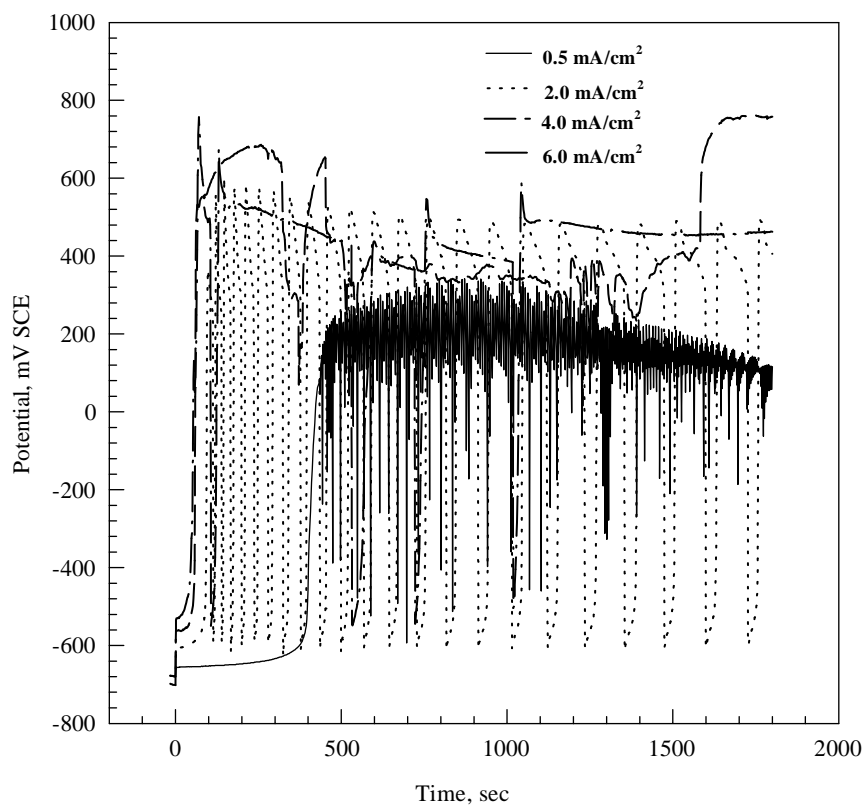


Fig. 10. Potential vs. time at pH 4.0 and $T = 45\text{ }^{\circ}\text{C}$.

Fig. 11. Potential vs. time at pH 4.0 and $T = 55^{\circ}\text{C}$.Fig. 12. Potential vs. time at pH 4.0 and $T = 65^{\circ}\text{C}$.

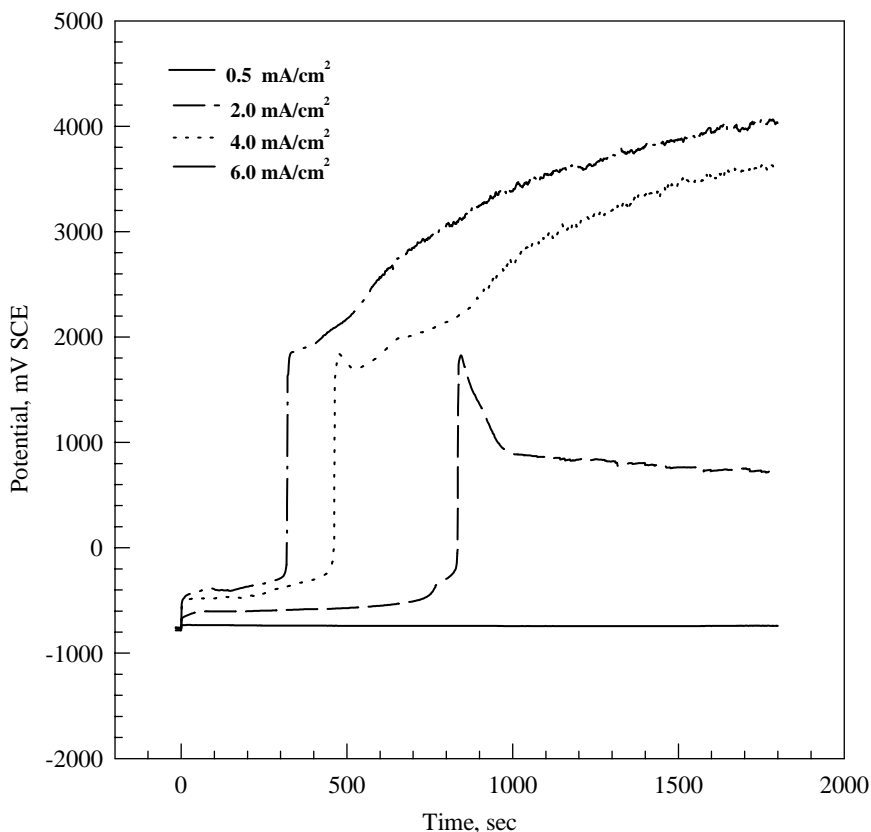
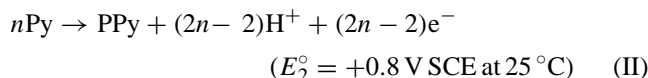
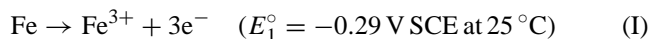


Fig. 13. Potential vs. time at pH 7.0 and $T = 25^{\circ}\text{C}$.

electrochemical reactions:



When a desired current is applied, the iron electrode undergoes dissolution according to reaction (I), which makes the surface active and renders reaction (II) difficult/impossible. At lower temperature, it takes a while to make a stable passive film on the surface. The stable surface allows the formation of polypyrrole.

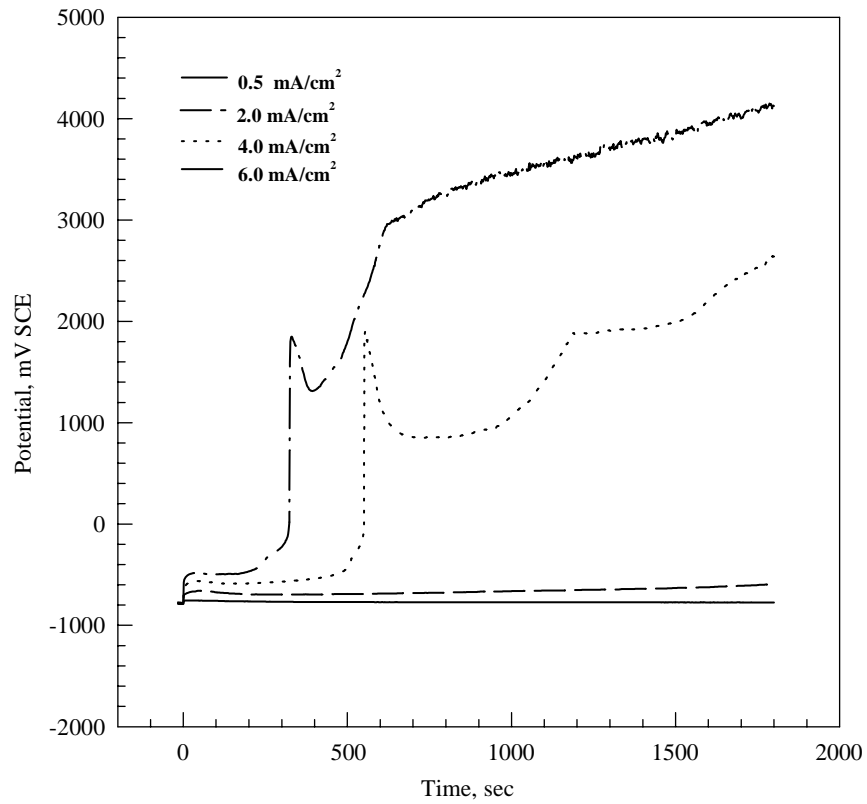
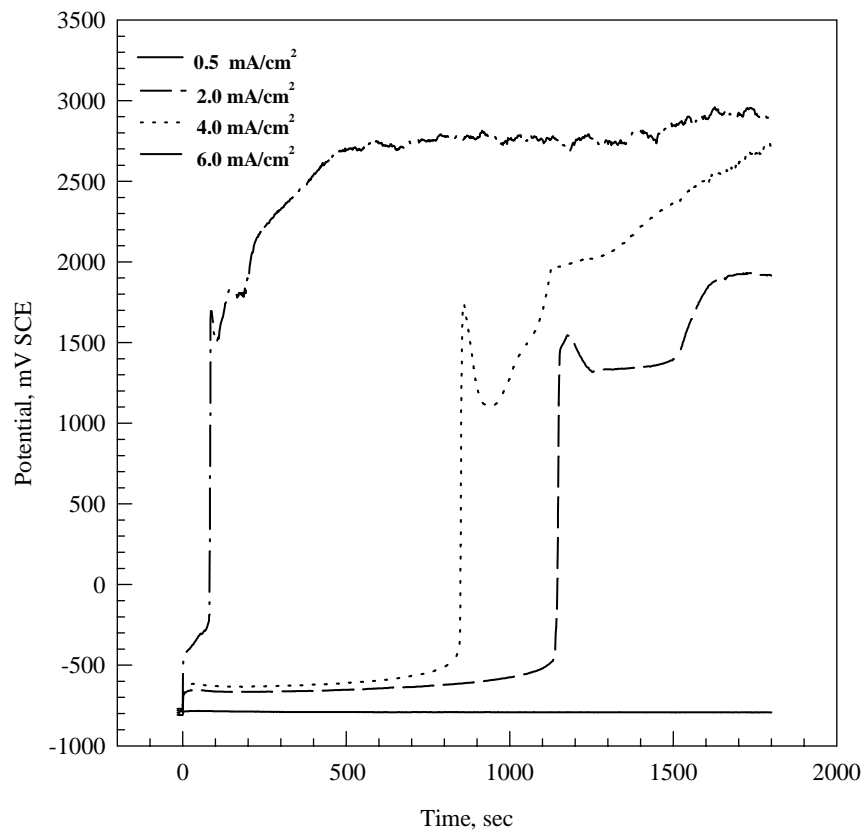
At higher temperatures, the rates of both the reactions accelerate but it seems that the kinetics of reaction (I) improves better than that of reaction (II). Consequently, a passive film is formed rapidly which allows reaction (II) to proceed and the potential rises quickly (the potential of reaction (II) is much higher). However reaction (I) does not terminate and causes the break down of newly formed polypyrrole layer. Reaction (I) dominates now and the potential of the electrode drops quickly. Once the surface becomes again temporarily passive, reaction (II) dominates. In this fashion reactions (I) and (II) dominate in turns causing observable oscillations in electrode potential. This unstable behaviors continues if the rates of these reactions are fast and comparable, e.g. at

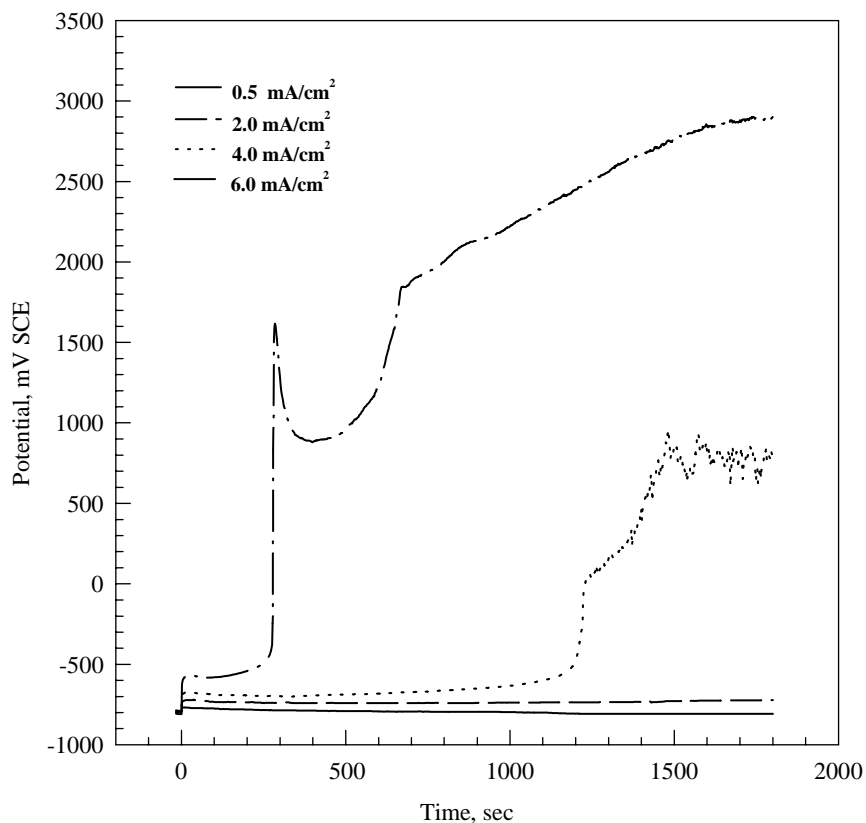
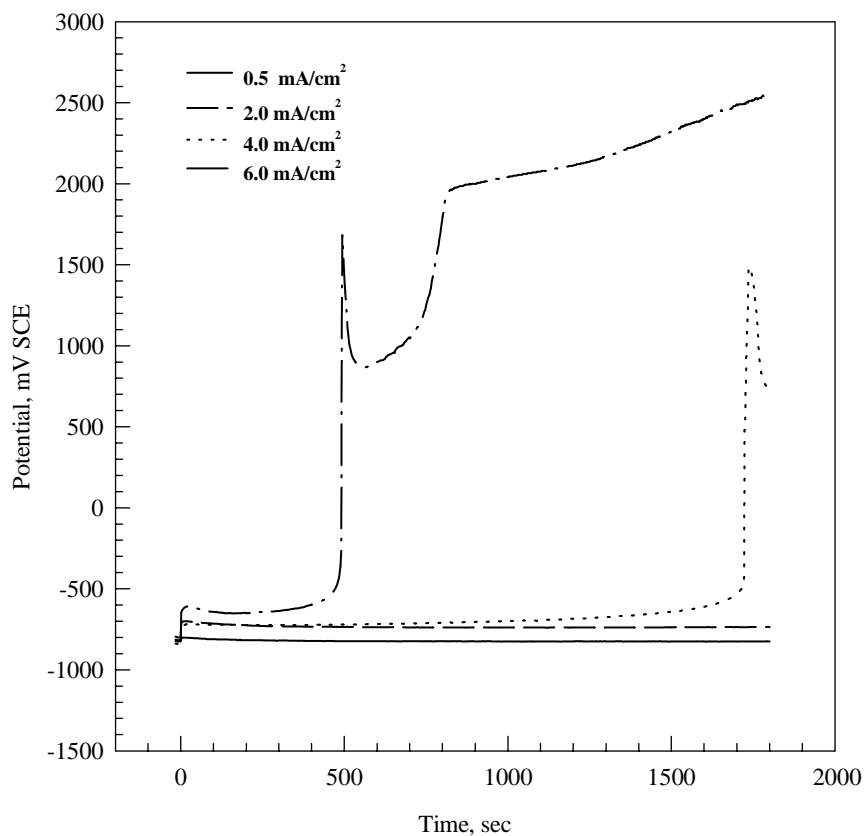
2.0 mA/cm², pH 2, 55 °C, at 4.0 mA/cm², pH 2, 65 °C or at 2.0 mA/cm², pH 4, 65 °C.

In some cases, the surface becomes passive and stable after some oscillations and normal deposition of polypyrrole takes place, e.g. at 0.5 mA/cm², pH 2, 35 °C, at 0.5 mA/cm², pH 2, 45 °C, at 0.5 mA/cm², pH 2, 55 °C, at 0.5 mA/cm², pH 2, 65 °C, at 2.0 mA/cm², pH 2, 65 °C, at 6.0 mA/cm², pH 2, 65 °C, at 0.5 mA/cm², pH 4, 65 °C, at 4.0 mA/cm², pH 4, 65 °C and at 6.0 mA/cm², pH 4, 65 °C. When pH is higher (i.e. 4.0) dissolution is slow that causes increase in induction time. In these cases only few or no oscillations were observed in the duration of experiment, e.g. at 0.5 mA/cm², pH 4, 35 °C and at 0.5 mA/cm², pH 4, 45 °C and at 0.5 mA/cm², pH 4, 55 °C.

3.2. In neutral and alkaline media

Figs. 13–17 exhibit chronopotentiometric plots for polypyrrole deposition in solution of oxalic acid neutralized by NaHCO₃ to desired pH. The figures correspond to temperatures 25, 35, 45, 55 and 65 °C. The deposition was not perceptible for current densities of 0.5 and 2.0 mA/cm² at 25 °C. Observable films of poor quality were obtained at 4.0 and 6.0 mA/cm². Compared to deposition in acidic media, in neutral media it requires generally higher passivation time. This is because of slower iron dissolution reaction.

Fig. 14. Potential vs. time at pH 7.0 and $T = 35^{\circ}\text{C}$.Fig. 15. Potential vs. time at pH 7.0 and $T = 45^{\circ}\text{C}$.

Fig. 16. Potential vs. time at pH 7.0 and $T = 55^{\circ}\text{C}$.Fig. 17. Potential vs. time at pH 7.0 and $T = 65^{\circ}\text{C}$.

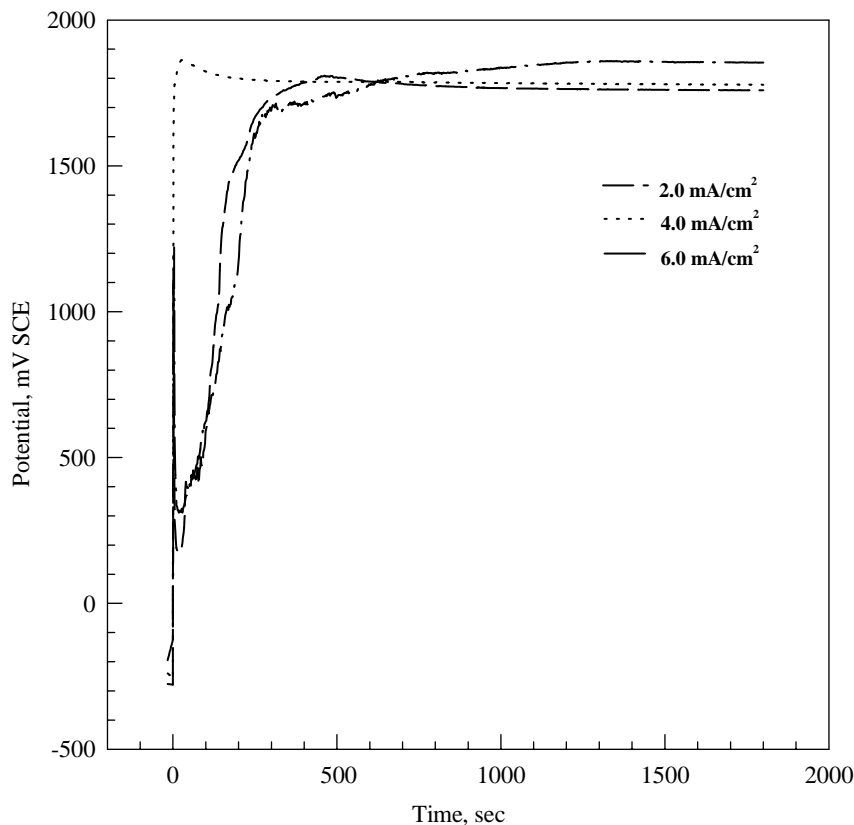


Fig. 18. Potential vs. time at pH 8.5 and $T = 25\text{ }^{\circ}\text{C}$.

The passivation time at 0.5 mA/cm^2 was more than the experiment time and therefore the jump in the potential to pyrrole oxidation potential was not observed. Another distinct feature of these plots is increasing potential with the passage of time. At higher temperatures the trends are similar except that in some cases it takes still longer to passivate the surface. The values of induction time are listed in Table 2. At $25\text{ }^{\circ}\text{C}$, when the applied current density was 0.5 or 2.0 mA/cm^2 , no good deposition was observed. Increasing the current densities to 4.0 or 6.0 mA/cm^2 would give better and thicker deposition of polypyrrole. The current density is inversely proportional to the induction time as in acidic medium. Fig. 13 shows that at low current density the surface needs much more time than that at high current density.

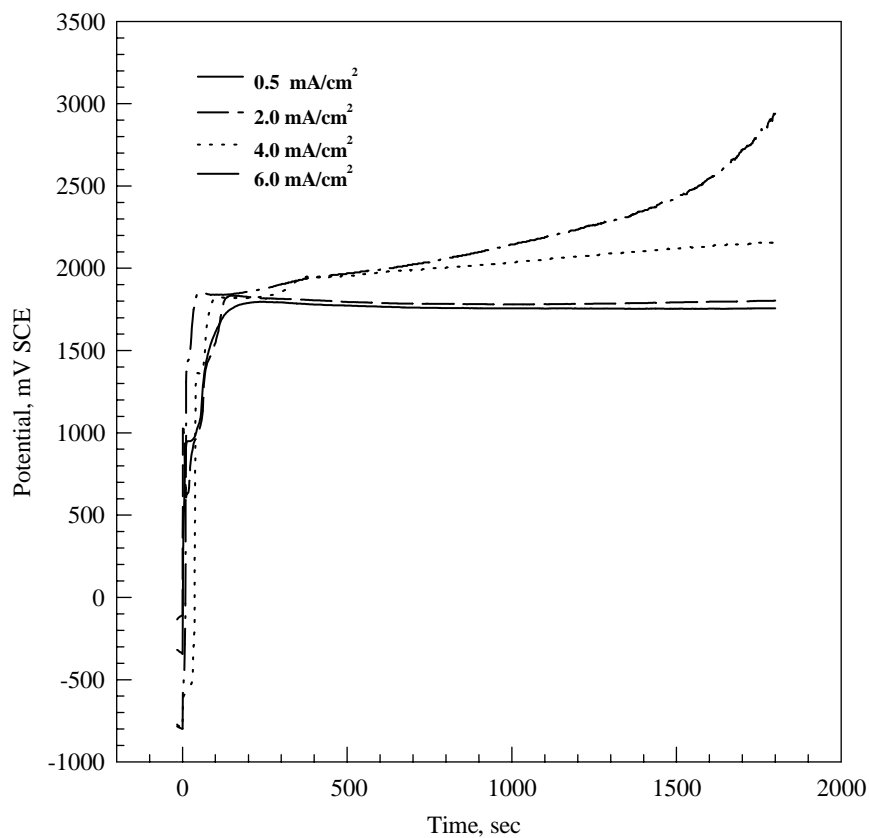
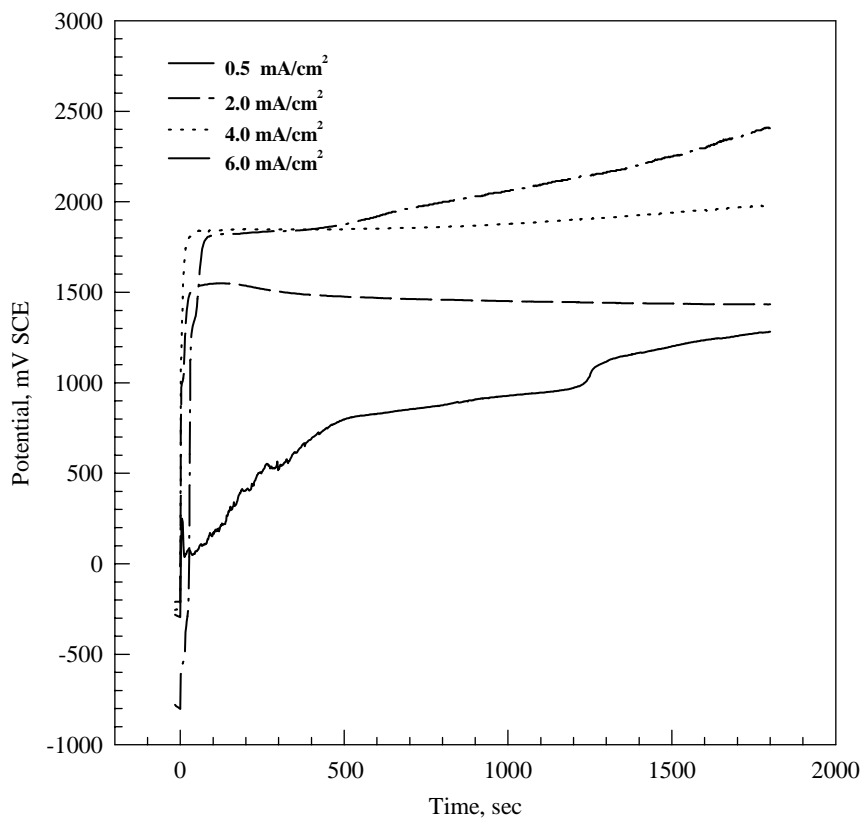
At higher temperatures, the potential–time plots showed the same trend as that at $25\text{ }^{\circ}\text{C}$. For the same applied current density, the deposition was not enhanced by increasing the temperature. When the applied current density was 0.5 or 2.0 mA/cm^2 , the induction time was constant even when the temperature increased. Increasing the temperature required longer time for the surface to be passivated when the current densities increased to 4.0 or 6.0 mA/cm^2 . Since the corrosion rate is low at pH 7.0, it takes longer time to achieve the required passivation for initiation of polypyrrole oxidation. For example, at current density of 4.0 mA/cm^2 , the induction

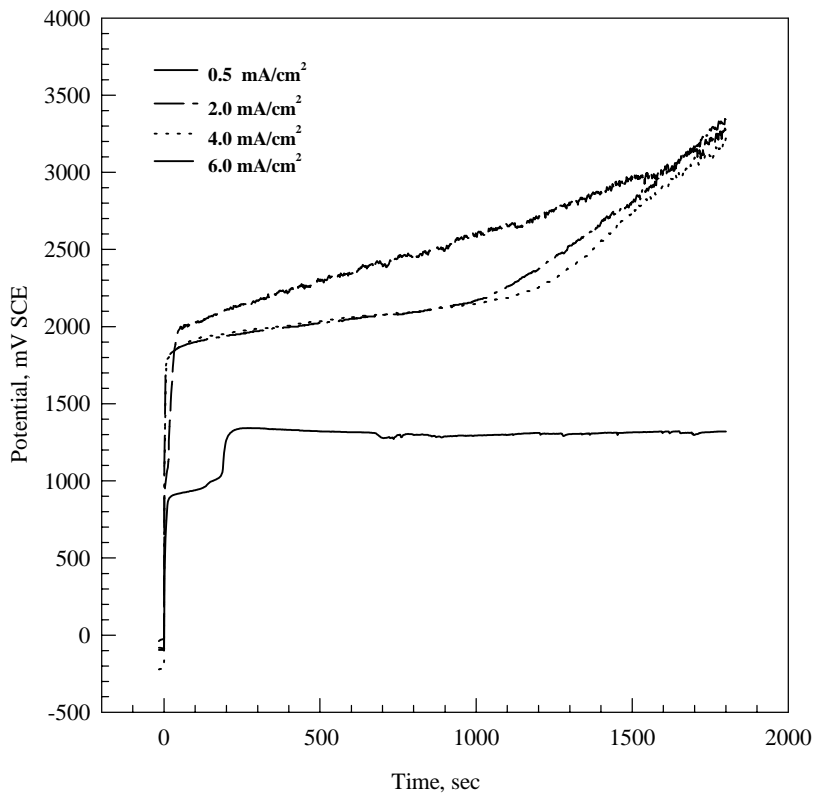
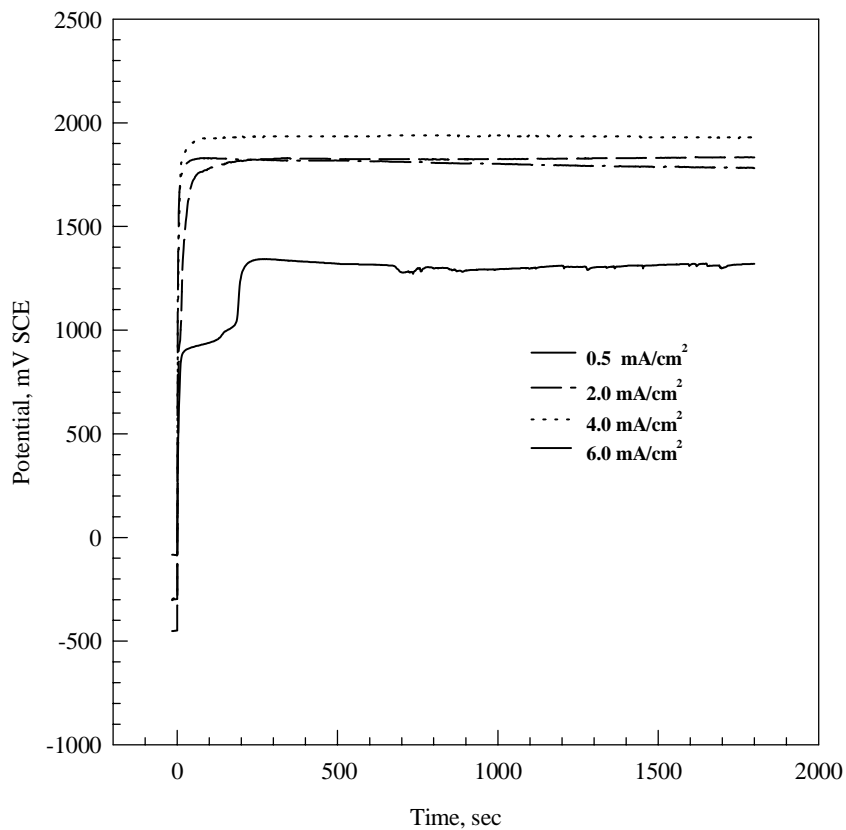
time was about 450 s at $25\text{ }^{\circ}\text{C}$, while it increased to 1715 s at $65\text{ }^{\circ}\text{C}$.

Electropolymerization in alkaline media was markedly different from neutral and acidic media as shown in Figs. 18–22. The figures do not show any induction time. This is because of readily formed passive film at the application of anodic potential in alkaline medium. This is the reason these curve only exhibit polymerization potential. Since there is no iron dissolution reaction, the potential does not undergo any oscillation. At $25\text{ }^{\circ}\text{C}$, no good deposition was observed at applied current densities of 0.5 and 2.0 mA/cm^2 . Increasing the current density increased the polymerization rate and better and compact films were formed.

It appears that for the same applied current density, increasing the temperature would result into adherent, smoother and better polypyrrole film. Apparently, in alkaline medium the polymerization rate was higher than the dissolution rate as temperature increased. Films obtained at high temperature were better than these obtained at room temperature.

The oxidation potential of pyrrole in alkaline medium was much higher than that in acidic medium for the same applied current density even at high temperatures. The mechanism is not clear and the reproducibility of the potential–time curves was poor as mentioned by Su and Iroh [7].

Fig. 19. Potential vs. time at pH 8.5 and $T = 35^{\circ}\text{C}$.Fig. 20. Potential vs. time at pH 8.5 and $T = 45^{\circ}\text{C}$.

Fig. 21. Potential vs. time at pH 8.5 and $T = 55^{\circ}\text{C}$.Fig. 22. Potential vs. time at pH 8.5 and $T = 65^{\circ}\text{C}$.

4. Conclusions

The effect of temperature on electropolymerization of pyrrole on mild steel substrate in oxalic acid electrolyte has been studied. In acidic medium, the overall process is favored by lower reaction temperatures. Higher acidic pH make the depositions difficult. Oscillations in electrode potential were observed while galvanostatic electropolymerization at the combinations of higher temperature and lower current densities. This oscillatory phenomenon is explained on the basis of instability arising from the competition of iron dissolution and pyrrole oxidation reactions. Deposition was difficult in neutral medium and poor quality films were obtained when current density was increased. In alkaline medium, the pyrrole oxidation started without any induction delay. The film quality was better and the process was favored by higher temperatures. The effect of these parameters on the conductivity of resulting polypyrrole film will be very interesting. The measurements using impedance electroscopy are underway in our lab.

Acknowledgements

Facilities and financial assistance provided by King Fahd University of Petroleum Minerals under grant CHE/C-PROTECTION/227 are gratefully acknowledged.

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